THE VON AUWERS REARRANGEMENT IN THE NAPHTHALENE SERIES

BY

THOMAS GORE MILLER

A.B., Miami University, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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INTRODUCTION

The thermal, non-catalytic rearrangement of 1-alkylidene-4-dichloromethyl-4-methyl-2, 5-cyclohexadienes has been extensively studied by von Auwers and his associates (1). In this unique aliphatic-aromatic isomerization the dichloromethyl group is transferred from the 4-position to the α-carbon atom of the alkylidene side chain with attendant aromatization of the ring. Trichloromethyl groups were later found to behave in a similar fashion (2).

Preparation of the starting materials for these experiments, 4-dichloro methyl-4-methyl-2,5-cyclohexadienones, was accomplished by means of the Reimer-Tiemann reaction on various para-substituted phenols.

This investigation was undertaken in order to explore the possibility of extending the von Auwers rearrangement to the naphthalene series and to examine the behavior of different types of alkylidenedihydronaphthalenes.

DISCUSSION OF RESULTS

The von Auwers rearrangement has been realized in the naphthalene series. 4-Methyl-1-naphthol was converted to 4-dichloromethyl-4-methyl-1-keto-1,4-dihydronaphthalene by the Reimer-Tiemann reaction. This cyclic ketone by treatment with ethylmagnesium bromide gave 1-ethylidene-4-dichloromethyl-4-methyl-1,4-dihydronaphthalene which isomerized to 1,1-dichloro-2(4-methyl-1-naphthyl) propane when heated to 150°. The structure of the rearrangement product was proved by an independent synthesis. 4-Methyl-1-aceto-naphthone was converted to β-methyl-β-(4-methyl-1-naphthyl) glycidic ester and thence, by hydrolysis of the ester and decarboxylation of the acid, to 2-(4-methyl-1-naphthyl) propanone. When treated with phosphorus pentachloride this aldehyde yielded 1,1-dichloro-2(4-methyl-1-naphthyl) propane.

5-Acenaphthenol gave a dichloromethyl ketone, 2a-dichloromethyl-5-keto-2a,5-dihydroacenaphthene, under the conditions of the Reimer-Tiemann reaction. The alkylidene compound obtained from this ketone by means of ethylmagnesium bromide did not isomerize when heated, but polymerized instead.

Two 4-allyl-1-naphthols were prepared and treated with chloroform and sodium hydroxide. In neither case could an appreciable amount of a neutral ketone be isolated. 4-Allyl-2-propyl-1-naphthol was prepared by Claisen rearrangement of 1-allyloxy-2-propylnaphthalene. 4-Allyl-1-naphthol was synthesized through the following series of compounds: 1-hydroxy-2-naphthoic acid, methyl 1-hydroxy-2-naphthoate, methyl 1-allyloxy-2-naphthoate, methyl 4-allyl-1-hydroxy-2-naphthoate, 4-allyl-1-hydroxy-2-naphthoic acid, 4-allyl-1-naphthol.

Alkylidene compounds were prepared by the action of ethyllithium and butyllithium on 1-dichloromethyl-1-methyl-2-keto-1,2-dihydronaphthalene and 1-allyl-1-methyl-2-keto-1,2-dihydronaphthalene (3). Normal addition by the organolithium reagents was accompanied by approximately 20 per cent of conjugate addition to give ketones. These alkylidene compounds did not undergo the von Auwers rearrangement when heated, but polymerized instead. The 1-methyl-2-naphthol used to prepare 1-dichloromethyl-1-methyl-2-keto-1,2-dihydronaphthalene was synthesized by a new route. 1-Piperidyl methyl-2-naphthol when treated with acetic anhydride gave 2-acetoxy-1-(acetoxymethyl)naphthalene. This benzyl-type ester was converted by simultaneous hydrogenolysis-alcoholysis to 1-methyl-2-naphthol.

An experiment was performed in which a cyano group was given an opportunity to migrate as do dichloromethyl groups in properly substituted alkylidenecyclohexadienes. α-Phenylpropionitrile was cyanoethylated to give α-methyl-α-phenylglutaronitrile, but the primary cyano group could not be selectively hydrolyzed to yield the desired acid. A Michael condensation between α-phenylpropionitrile and methyl acrylate gave the cyano ester which was readily hydrolyzed to γ-cyano-γ-phenylvaleric acid. Cyclization of this

acid and bromination and dehydrobromination of the ketone gave 4-cyano-4-methyl-1-keto-1,4-dihydronaphthalene. This ketone when treated with ethylmagnesium bromide yielded a mixture of the normal and conjugate addition products. The mixture was heated to 180° and distilled. The distillate consisted of 1-ethyl-4-methylnaphthalene and 4-cyano-4-methyl-3-ethyl-1-keto-1,2,3,4-tetrahydronaphthalene, the 1,4 adduct.

A mechanism was proposed for the von Auwers rearrangement which involves dissociation into a dichloromethyl ion and carbonium ion. In the recombination the carbonium ion behaves as though it were aromatic, the charge being associated with the α-carbon atom of the ethylenic side chain.

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VITA

The author was born on November 3, 1924, in Greenfield, Ohio, where he received his elementary and high school education. He entered Miami University in September, 1942, and remained there until his induction into the Army in March, 1943. He reentered Miami University in February, 1946, and was graduated with the Bachelor of Arts Degree in June, 1948. In September, 1948, he entered the Graduate School of the University of Illinois where he received the Master of Science degree in 1949. He held teaching assistantships in inorganic chemistry during 1948-1951 and a research assistantship during the summer of 1951.

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